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(54) High-temperature oxide superconductor.

(57) The present invention provides a high-temperature oxide superconductor which comprises an oxide expressed as $(Bi_{1-x}A_x)$ - By - Cz -Cu oxide (where A is Sb and/or As; B and C are elements different from each other, each being one or more elements selected from Be, Mg, Ca, Sr and Ba; and $0 \leq x < 1$, $0 < y \leq 5$ and $0 < z \leq 5$).

According to the present invention, it is possible to manufacture a high-temperature oxide superconductor having a transition temperature of over 100 K and not containing a rare-earth element at all, and to manufacture a superconductor excellent in reliability and stability more easily than conventional superconductors such as Y-Ba type superconductors.

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HIGH-TEMPERATURE OXIDE SUPERCONDUCTOR

The present invention relates to a high-temperature oxide superconductor, and more particularly, to a high-temperature oxide superconductor which does not contain a rare-earth element and has a very high superconductivity transition temperature of over 100K.

High-temperature oxide superconductors are attracting attention as having a high superconductivity transistion temperature far exceeding that of superconductors comprising an alloy such as Nb-Ti, Nb_3Sn or V_3Ga or an intermetallic compound, and are expected to be suitable for wires, tapes and disk-shaped sinters in such a wide range of areas from strong electricity areas such as superconductor magnets for producing high magnetic fields and for superconductive magnetic energy storage to various materials for cryoelectronic components such as the Josephson device and SQUID and to sheet materials for magnetic shielding.

Known high-temperature oxide superconductors conventionally include 30K-class $(La_{1-x}\ Ba_x)\ CuO_4$ and 40K-class superconductors as represented by $(La_{1-x}Sr_x)\ CuO_4$ as the first-generation materials, followed by the more recent appearance of a 90K-class oxide superconductor represented by $YBa_2Cu_3O_{7-\delta}$. The keen development competition thereafter revealed that all the materials which include the replacement of Y (yttrium) of $YBa_2Cu_3O_{7-\delta}$ by another rare-earth element (other than Sc, Ce, Pr, Pm and Tb) are superconductors having a 90K-class superconductivity transition temperature (Tc), and have been generally recognized as second-generation high-temperature oxide superconductors.

These Y-Ba type oxide superconductors however pose problems in that their properties are very sensitive to lack of oxygen (δ) and superconductivity cannot be achieved unless structural transformation of tetragonal and rhombic crystal grains is subtly controlled during the process of heat treatment i.e., it is very difficult to conduct proper heat treatment.

Furthermore, these conventional superconductors are unstable relative to moisture and carbon dioxide gas because of the presence of a rare-earth element, thus resulting in many different problems in the manufacture of high-performance wires, thin films or the like. In addition, rare-earth elements are uncertain in supply because of the maldistribution of resources throughout the world, leading to high prices.

Since the appearance of these Y-Ba type high-temperature oxide superconductors, research and development efforts have been actively in progress throughout the whole world in an attempt to achieve a higher Tc, and materials having a Tc of 200K, room temperature or even in excess of 300K have been announced, although none of these materials have as yet been recognized due to the lack of established evidence of superconductivity.

There is therefore a strong demand for a high-temperature oxide superconductor superior to Y-Ba type superconductors.

The present invention was made in view of the circumstances as described above. An object of the present invention is to overcome the problems involved in the conventional oxide superconductors and provide a new high-temperature oxide superconductor of the 100K to 100 K class which is stable and permits easy heat treatment, without the use of a rare-earth element.

This and other objects, features and advantages of the invention will become more apparent in the detailed description with reference to the drawings and examples which follow.

Reference will be made to the accompanying drawings in which:

Figure 1 is an electric resistance-temperature curve diagram illustrating an embodiment of the present invention; and

Figure 2 is a superconductivity transition curve diagram obtained through measurement of AC magnetization rate.

The present invention provides a high-temperature oxide superconductor which comprises an oxide expressed as $(Bi_{1-x}\ A_x)$ - B_y - C_z - Cu oxide (wherein, A is Sb and/or As; B and C are elements which are different from each other, each being one or more elements selected from Be, Mg, Ca, Sr and Ba; $0 \leq x < 1$, $0 < y \leq 5$ and $0 < z \leq 5$).

In an oxide of this chemical composition, it is essential to combine Bi (bismuth) and Cu (copper), as well as two or more elements selected from Be, Mg, Ca, Sr and Ba. Sb and As, which fall within the same periodic group (group Vb) as Bi, may be used as partial substitution elements of Bi. Although any of Be, Mg, Ca, Sr and Ba may be combined, the combination of Sr and Ca is particularly preferable.

The oxide of the present invention should preferably have a chemical composition of $(Bi_{1-x}A_x)$ - B_y -C_z - $Cu_{2-\delta}$ -0 und r the conditions of, for example, $0 \leq x < 1$, $0 < y \leq 5$, $0 < z \leq 5$ and $-1 \leq \delta$, and more preferably, $0.1 \leq y \leq 5$, and $0.1 \leq z \leq 5$. A composition with y and z of under 0.1 and over 5 leads to a

decreased transition temperature (Tc). A composition of the form $(Bi_{1-x}\ A_x)$- B - C - Cu oxide is also preferred (wherein A, B, C and x are as hereinbefore defined). Further preferably, a composition with x = 0, Sr and Ca selected as B and C, and approximately y = z = 1 and Cu = 2 gives an excellent superconductivity.

After blending compounds such as oxides, carbides and carbonates of the component elements at prescribed ratios and mixing them sufficiently, the oxide of the present invention may be calcined at a temperature of from about 700 to 900 °C, preferably 750 to 850 °c, for a period of from a few, for example 2, 3 or 4 hours, to 20 hours, preferably 5-15 hours, more preferably 5-10 hours, crushed, formed into pellets, and then sintered at a temperature of from about 800 to 900 °C, preferably 830-860 °C. It is needless to mention that there is no particular limitation in temperature and other conditions.

In this sintering, it is desirable to keep the oxide in a semi-molten state. Conventional cooling may be applied after sintering. It is not necessary to closely control these heat treatment processes as in the case of a conventional Y-Ba type oxide. A high superconductivity is achievable also on quenching.

The oxide superconductor of the present invention shows a transition temperature of over 105K and is excellent in reliability and stability. The high-temperature superconductor is easily available with a high reproducibility because the superconductivity of the oxide is not sensitive to heat treatment.

to oxide superconductor of the present invention can be easily formed not only into a sinter but also into a thin film. The thus formed sinter has a high density and is expected to have a high critical current density (Jc).

Examples 1 to 13

Bi_2O_3,$SrCO_3$, $CaCO_3$ and CuO powder materials were blended in ratios of the respective metal elements as shown in Table 1, and mixed sufficiently. The mixture was calcined at a temperature of from 800 to 880 °C for from five to ten hours, and formed into disk-shaped pellets having a diameter of 20 mm and a thickness of about 2 mm under a pressure of 2 tons/cm² by means of a cold press. These pellets were fired in the open air at a temperature of from 800 to 900 °C for ten hours, and then furnace-cooled to room temperature for from five to ten hours.

Strip-shaped specimens having a width of about 3 mm and a length of 20 mm were cut out of these pellets to measure electric resistance and the superconductivity transition temperature Tc by the electromagnetic induction method.

For the Bi_1 - Sr_1 - Ca_1 - Cu_2 oxide, as shown in Figure 1, the superconductivity transition temperature starts at about 115K, and electric resistance becomes completely null at 105K.

The result shown in Figure 2 is in good agreement with this observation: particularly a large change in magnetization rate represents the perfect diamagnetism (Meissner effects) unique to a superconductor.

The result of measurement of the transition temperature shown in Table 1 also suggests that the oxide of the present invention is a new superconductor having a Tc of over 100K.

Table 1

Example No.	Composition (atomic ratio)				Superconductivity transition temperatur (K)		
	Bi	Sr	Ca	Cu	Start point	Middle point	End point
1	1	1	1	2	115	108	105
2	1	1	1	3	115	110	107
3	1	1	1	4	115	110	102
4	1	1	1	5	115	108	102
5	1	1	1	6	115	108	102
6	1	1	1	9	115	108	102
7	1	1	0.5	3	90	80	68
8	1	1	0.25	3	95	80	65
9	1	2	1	4	115	80	68
10	1	1	2	4	90	80	68
11	1	3	2	6	90	80	68
12	1	1	0.05	2	20K > T > 4K		
13	1	2	0.05	4	20K > T > 4K		

Example 14 to 16

Another superconductor comprising a Bi- Sb -Sr - Ba - Ca - Cu oxide was prepared in the same manner as in Examples 1 to 13. By the change in electric resistance, a 100K-class superconductor was obtained.

Similarly, a Bi - As - Ba - Mg - Ca - Cu oxide and a Bi - Be - Ca - Cu oxide were prepared.

A 100K-class oxide superconductor having a chemical composition quite different from those of the conventional ones is provided by the present invention. It has a very remarkable industrial and academic significance as a superconductor not containing a rare-earth element at all.

As compared with the conventional ones, there is available a high-temperature superconductor excellent in reliability and stability, easily and at a high reproducibility because of non-sensitivity of superconductivity to a series of manufacturing and heat treatment processes such as calcination, sintering and cooling. This gives very important advantages for forming products into for example wires and thin films. The high density of the sinter gives a high Jc.

The present invention, not requiring rare-earth elements maldistributed on the earth, is far more advantageous than the conventional ones in terms of resource supply and provides industrially very useful effects.

The present invention also provides a solution to the problem of resources since liquefied nitrogen may be used as a cooling medium.

Claims

1. A high-temperature oxide superconductor which comprises an oxide expressed as: $(Bi_{1-x}\ A_x)$ - B_y - C_z - Cu oxide (wherein A is Sb and/or As; B and C are elements which are different from each other, each being one or more elements selected from Be, Mg, Ca, Sr and Ba; and $0 \leq x < 1$, $0 < y \leq 5$ and $0 < z \leq 5$).

2. A superconductor as claimed in claim 1, which comprises an oxide expressed as $(Bi_{1-x}\ A_x)$ - B_y- C_z - Cu_2 - δ oxide (wherein A, B, C, x, y and z are as defined in claim 1 and $-1 \leq \delta$)

3. A superconductor as claimed in claim 1 or claim 2 wherein $0.1 \leq y \leq 5$ and $0.1 \leq z \leq 5$.

4. A superconductor as claimed in any of claims 1 to 3, which comprises an oxide expressed as $(Bi_{1-x}\ A_x)$ - B - C - Cu oxide (wherein A, B, C and x are as defined in claim 1).

5. A superconductor as claimed in any of the preceding claims wherein x = 0, and y and z are each approximately 1.

6. A superconductor as claimed in claim 2 wherein x = 0, y and z are each approximately 1 and δ = 0.

7. A superconductor as claimed in any one of claims 1 to 6 wherein B and C are elements which are different from each other, and being either Sr or Ca.

8. A process for preparing a superconductor as claimed in claim 1, which comprises blending together compounds of Bi, Cu, and elements A, B and/or C (wherein A, B and C are as defined in claim 1) in the desired ratios, calcining the blend at a temperature of from about 700 °C to 900 °C for a period of not more than 20 hours, crushing the thus-obtained product and forming the product into pellets, and sintering at a temperature of from 800 to 900 °C.

FIG.1

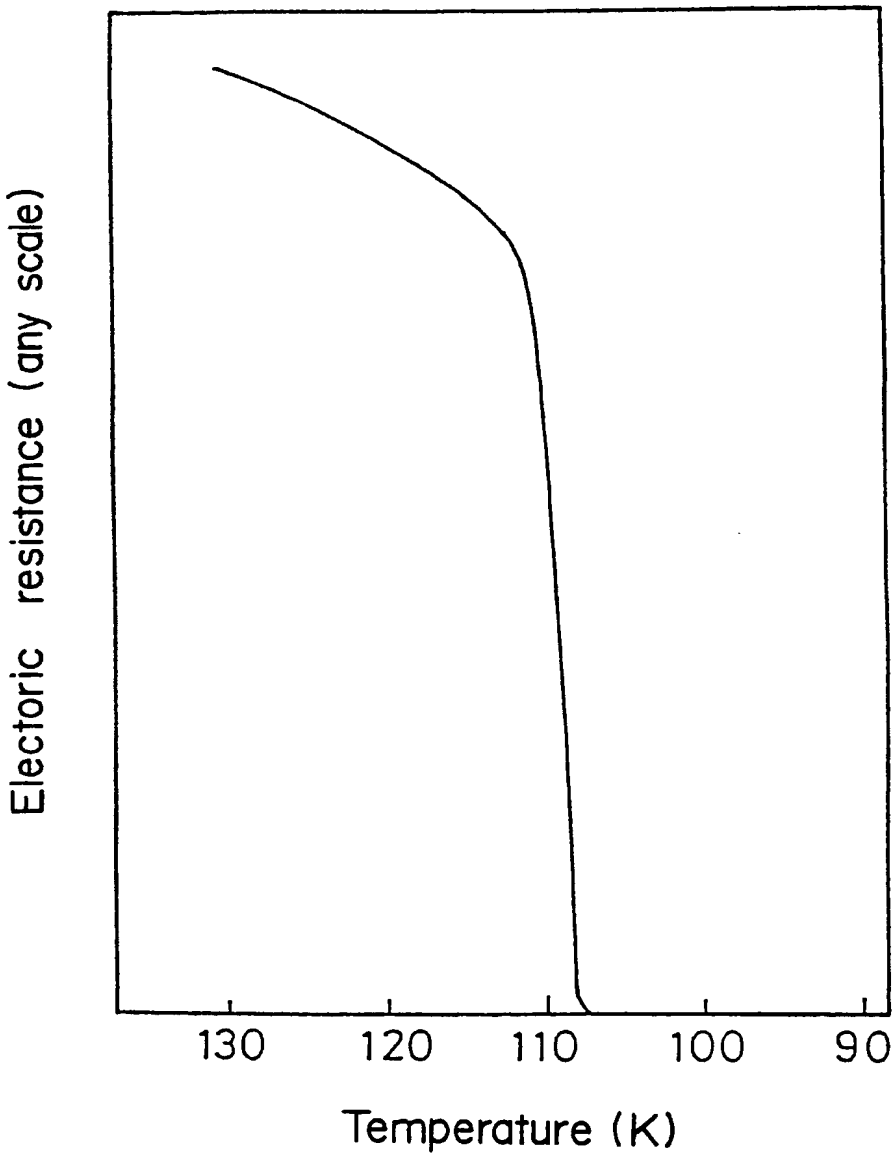
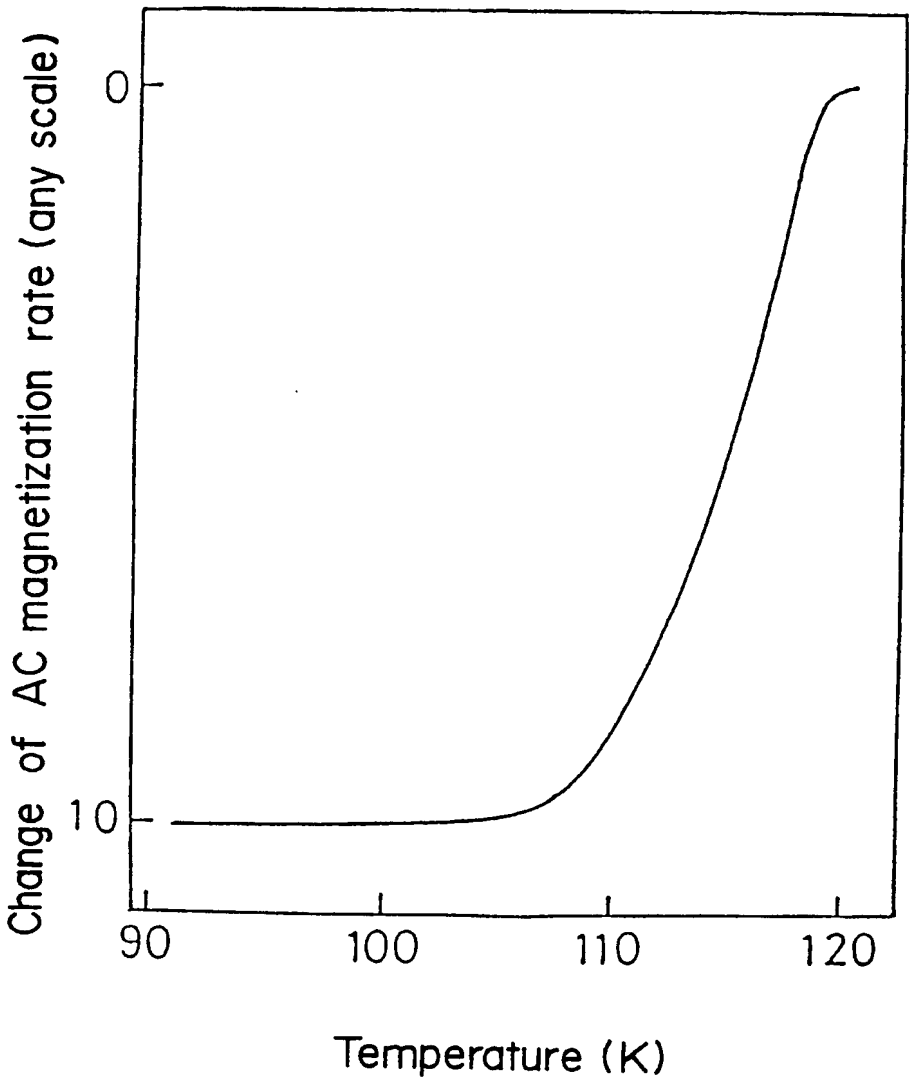

Electoric resistance (any scale)
130
120
110
100
90
Temperature (K)

FIG. 2


Change of AC magnetization rate (any scale)
0
10
90
100
110
120
Temperature (K)